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(54) Curable fluoroelastomeric compositions.

(57) Curable fluoroelastomeric compositions employable for preparing fuel hoses or O-rings for injectors comprising:

A) 100 phr (parts) copolymers or terpolymers based on VDF with a content in fluorine of at least 67% by weight, the VDF being comprised from 30 to 50% by weight, from 20 to 60% by weight of HFP optionally other monomeric units deriving from a monomer having ethylene unsaturation; the sum of the comonomers being 100;

B) 1 to 5 phr of an adduct between an accelerator and a curing agent in molar ratio from 1:2 to 1:5, the accelerator being an anionic-organic compound having a positive charge, the curing agent being a di- or polyhydroxy or di- or polythiol compound; the adduct being obtained by melting of the reaction product between accelerator and curing agent in the indicated molar ratios, or by melting of the adduct mixture 1:1 added with the curing agent in the indicated amounts.

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The present invention relates to curable vinylidene-fluoride copolymers having a high content in fluorine, the other comonomers deriving from fluorinated monomers with ethylene unsaturation.

More detail the present invention relates in particular to fluoroelastomeric copolymers based on vinylidene-fluoride (VDF), hexafluoropropene (HFP), optionally in the presence of one or more comonomers ethylenically unsaturated, the F amount being higher than 67% by weight.

More particularly the invention relates to fluoroelastomeric copolymers based on VDF suitable to the preparation of fuel hoses and shaft seals.

It is known that for the preparation of these articles, fluoroelastomeric polymers are required having good resistance to motor oils and/or to petrols containing polar substances, in particular alcohols.

This property must be combined with good elastomeric properties such as compression set and good mechanical properties and good processability in molding both by compression, by injection and by extrusion.

The same copolymers can be also used for preparing O-rings used in the injectors coming into contact with petrols and/oil containing polar substances.

It is known making articles based on VDF, HFP and tetrafluoroethylene (TFE), optionally in the presence of perfluoroalkylvinylethers (PAVE), using the peroxidic curing. The disadvantage is that the compression set obtained are poor and the removal from molds is unsatisfactory.

It is also known from the previous patent application of the Applicant, EP 525687, to carry out the ionic curing with known accelerators and curing agents. The drawback is that these products show mechanical properties lower than the products cured with peroxides.

To obviate these inconveniences in the art it is known to use also processing aids such as sulphones or sulphoxides. The drawback is that the addition of these products, even though they lead to an improved rubber processing, worsen the mechanical properties and depending on the accelerating system worsen also the compression set.

It is known, moreover, that the elastomeric polymers having high content of fluorine show a bad processability due to the high viscosity of the compound.

All the disadvantages of the copolymers based on VDF with low content in fluorine (less than 67% by weight), are even more stressed in case of VDF copolymers having high content in fluorine, as indicated above.

In case of copolymers or terpolymers, indeed, having high content in fluorine, the crosslinking is even more difficult and wherefore the mechanical and elastic properties and the processability of the article result poor.

It has surprisingly and unexpectedly been found that it is possible to prepare fluoroelastomeric polymers based on VDF having a very good combination of

- high mechanical properties,
- low compression set,
- low viscosity of the compound such as to allow an easy processing both by compression, by injection and by extrusion,
- high resistance to oils and to petrols containing polar substances, such as alcohols or ethers.

This has been made possible by using ionic curing with a particular accelerating/curing system as herein defined.

Object of the present invention are curable fluoroelastomeric compositions comprising

A) 100 phr (parts) copolymers of terpolymers based on VDF having a content in fluorine of at least 67% by weight, the VDF being comprised from 30 to 50% by weight, from 20 to 60% by weight of HFP, optionally other mono-meric units deriving from a monomer having ethylene unsaturation; the sum of the comonomers being 100. In case of copolymers, the VDF ranges from 40 to 50 and HFP ranges from 50 to 60% by weight. The other comonomers are preferably from 0 to 30% of TFE and from 0 to 40% of perfluoroalkylvinylethers, preferably 0-20%;

B) 1 to 5 phr, preferably 2 to 4.5, of an adduct between an accelerator and a curing agent in molar ratio from 1:2 to 1:5, preferably 1:2 to 1:3, the accelerator being an onio-organic compound having a positive charge, the curing agent being a di- or polyhydroxy or di- or polythiol compound; the adduct being obtained by melting of the reaction product between accelerator and curing agent in the indicated molar ratios, or by melting of the adduct 1:1 added with the curing agent in the amounts to reach the 1:2 to 1:5 adduct; optionally

C) the accelerator indicated in B) in amounts from 0.05 to 0.5 phr.

The onium compound used as accelerator in B) and C) and forming the adduct cation is generally selected from the following classes:

I) aminophosphonium $[P(NR'R'')_n(R^1 R^2 R^3)_{4-n}]^+$ wherein n is an integer from 1 to 3; R', R'' and R¹ R² R³, equal or different from each other, are alkylic, cycloalkylic, aryllic, arylalkylic, xyalkylic or polyoxyalkylic groups having a free or esterified terminal -OH function; R' and R'' contain from 1 to 7 carbon atoms and can be linked each other so as to form an heterocyclic ring with the nitrogen atom while R¹, R², R³ equal

or different from each other contain from 1 to 18 carbon atoms;
 II) compounds having the formula



wherein Q is selected from nitrogen, phosphorus, arsenic, antimonium;
 III) compounds having formula:



wherein in II) and III) R^a, R^b, R^c, R^d are selected from alkyls, aryls, alkylaryls or their combinations, two of said free radicals can be linked each other and the Q or S atom can form an heterocyclic ring.

Preferred compounds are quaternary phosphonium compounds containing at least a phosphorus atom linked by four covalent simple bonds to four organic radicals, the organic radicals generally containing from 1 to 30 carbon atoms, preferably from 2 to 8. The organic radical, being linear or branched, can contain heteroatoms. Preferred compounds are triphenylbenzylphosphonium, tetrabutylphosphonium.

The accelerator can be also a blend of the compounds of the single classes I) to III), or of more compounds of the same class.

The anion forming the adduct must be a curing agent and is generally selected from the polyhydroxy or polythiol compounds comprising the following classes:

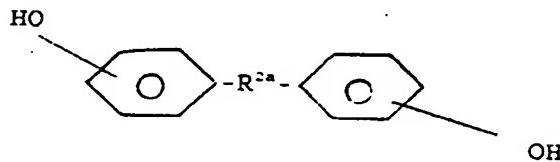
X1) A(BH)_m

wherein A is an arylene radical optionally substituted with alkylic groups, such radical including optionally alkyl groups has from 6 to 14 carbon atoms, B is oxygen or sulphur and m is equal to 2 or 3;

X2) HB-R^{4a}-BH

wherein R^{4a} is an alkylene or cycloalkylene radical optionally substituted with alkylic groups, such radical including optionally alkyl groups has from 6 to 18 carbon atoms and B is oxygen or sulphur;

X3)



wherein R^{2a} is -SO-, -SO₂-, -CO- or a linear or branched alkylene radical containing from 1 to 9 carbon atoms and wherein the H atoms can be partially or wholly substituted with F atoms;

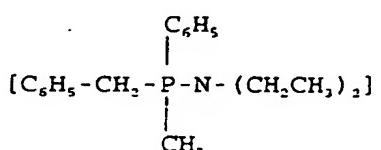
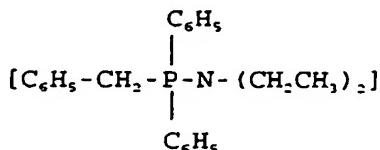
X4) HOCH₂-R^{3a}-CH₂OH

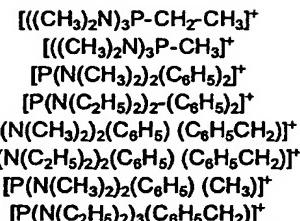
wherein R^{3a} is a perfluoropolyether or Polyfluoroether chain, the average molecular weight by number Mn being from 360 to 2,000.

The accelerators forming the cation are described in the art for instance in USP 4259463 for aminophosphonium compounds, in USP 3712877 for quaternary phosphonium salts, USP 3655727 for quaternary ammonium salts, in EP 337705 for class III).

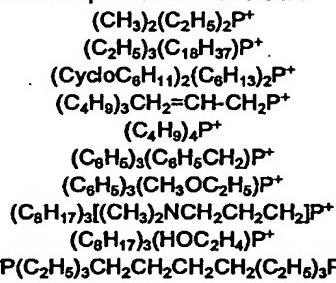
The preferred cations are those deriving from aminophosphonium wherein the phosphorus atom is linked to a nitrogen atom and the other three covalent bonds are formed by organic radicals wherein the carbon is linked to phosphorus.

The following compounds can be cited:





10 The compound 1,1-diphenyl-1-benzyl-N-diethyl-phosphoramine is particularly preferred.
 Among the quaternary phosphonium compounds it can be cited



15 Tetrabutyl phosphonium is particularly preferred.

Among anions the bisphenol compounds (class X3), wherein the R^{2a} radical is the perfluoroalkyl group from 3 to 7 carbon atoms, and the OH are in para position, are preferred. The most preferred compound is $\text{R}^{2a} = -\text{C}(\text{CF}_3)_2-$.

20 The adduct can be prepared as follows.

The polyhydroxy or polythiol compound is reacted, in aqueous solution or in a suitable solvent, for instance methanol, wherein the accelerator is soluble, in a first step, with a basic substance, for instance NaOH, KOH, $\text{Ca}(\text{OH})_2$ and $t\text{BuO}^\bullet\text{K}^+$, generally by using one equivalent gram of basic substance for mole of accelerator. The reaction product is then reacted in a second step with an accelerator salt, for instance a chloride. The desired salt precipitates. After filtering and drying, the product is melted which through cooling, solidifies in flakes or pellets giving the adduct utilized in the present invention. This solid form is particularly suitable for its handling and its compounding in the blends.

The polyhydroxy or polythiol compounds are used in molar ratios from 2:1 to 5:1 with respect to the accelerator.

25 35 Without being bound to any theory, it seems by IR spectra that the excess of polyhydroxy compound results linked to the cation also when this results in excess with respect to the stoichiometric, as it must be according to the present invention.

40 Tests carried out by the Applicant have shown that the adducts with excess of bisphenol with respect to the accelerator show superior properties if the amount of curing agent is added in excess during the adduct preparation or after the adduct achievement in molar ratios 1:1 between accelerator and curing agent, before bringing to melting the reaction mixture containing the excess of curing agent.

As a matter of fact, if the adduct in molar ratio 1:1 is prepared and the reaction product is melted and only afterwards the desired amount of curing agent is added, the improved results according to the present invention are not obtained.

45 The curing blend comprises moreover, in order to obtain the cured products through heating,
 a) one or more acceptors of inorganic acids selected among the ones known in ionic vulcanisation of vinylidene fluoride copolymers, in amounts 1-40 parts for 100 parts fluoroelastomeric copolymer;
 b) one or more basic compounds selected from those known in ionic vulcanisation of vinylidene fluoride copolymers, in amounts from 0.5 to 10 parts for 100 parts of fluoroelastomeric copolymer.

50 As also known, the basic compounds of point b) are usually selected from the group consisting of $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, metal salts of weak acids, such as for instance carbonates, benzoates, oxalates and phosphites of Ca, Sr, Ba, Na and K and mixtures of the aforesaid hydroxides with the abovesaid metal salts.

55 The composition according to the present invention commonly comprises other known components, such as fillers, for instance, carbon black, silica and dyes, generally from 5 to 30 phr; and processing adjuvants, for instance plasticizers, generally from 0.1 to 5 phr.

However an advantage according to the present invention consists in that optimum results are obtained without using processing adjuvants, such as sulphones, which generally lead to a worsening of the final properties depending on the used accelerating system.

The fluoroelastomeric copolymers, as said above, are vinylidenefluoride copolymers with one or more fluorinated monomers having ethylene unsaturation. In particular the copolymers of the present invention are VDF copolymers with hexafluoropropene.

Other comonomers having ethylene unsaturation which can be used are vinyl ethers (PAVE) in amounts from 0 to 40% by weight, preferably 0-20%. The preferred vinyl ethers are perfluoroalkylperfluorovinylethers, in particular perfluoromethylperfluorovinylether (MVE) and perfluoropropylperfluorovinylether. Utilizable perfluorovinylethers and perfluoroalkoxyvinylethers are described in USP 3291843.

Other comonomers which can be utilized in amounts from 0 to 30% are for instance tetrafluoroethylene and/or chlorotrifluoroethylene.

The olefinic monomers having up to 4°C are for instance selected from ethylene and propene, the preferred being ethylene (Et), and are used in amounts from 0 to 25% by weight, preferably from 0 to 10%.

The preferred copolymers forming the object of the present invention are characterized by the following preferable composition by weight of monomeric units:

15

	% by weight
VDF	40-50%
HFP	50-60%;

20

or by the composition:

25

	% by weight
VDF	30-50%
HFP	20-60%
TFE	10-30%;

30

or by the composition:

35

	% by weight
VDF	30-47%
HFP (hexafluoropropene)	20-40%
PAVE	3-20%
TFE	10-30%.

40

The copolymers of the invention combine a good chemical resistance with a high curing rate, essential requirement in transformation techniques such as injection molding.

Such copolymers are capable of meeting more and more severe marketing specifications, which require good resistance to alcohols and to petrols containing alcohols especially methanol.

45

The VDF copolymers containing olefins particularly suitable due to their high resistance to alcohols and to bases, in particular oils containing amines, contain preferably the following monomer units:

50

	% by weight
VDF	30-50%
HFP	20-58%
PAVE	0-40%
ethylene	2-15%
TFE	0-30%.

55

The fluoroelastomeric copolymers according to the present invention are prepared by emulsion polymer-

5 ization according to well known techniques, preferably in the presence of radicalic initiators such as for instance persulphates, perphosphates, alkalin or ammonium perborates or percarbonates, optionally in combination with reducing agents such as sulphites, bisulphites, hyposulphites, phosphites, hypophosphites of alkalin or ammonium metals, or in combination with ferrous, cupreous or silver salts, or of other easily oxidable metals. Such methods are described in Kirk Othmer, Encyclopaedia of Chemical Technology, vol. 8, pag. 500 and on, 1979. As polymerization methods can be used, in particular, the mass polymerization, that in solution of organic solvents and the one in emulsion or suspension in water.

10 Surfactants, such as for instance ammonium perfluoroctanoate or others known to be suitable in preparing fluoroelastomers can be present in the polymerization medium, for example ammonium perfluoro-octanoate.

15 Chain transfer agents can generally be used as molecular weight regulators. Among them ethyl acetate, ethyl malonate, iodided and/or brominated chain transfer agents, such as for instance the compounds having the general formula $Rf(I)_x(Br)_y$, wherein Rf = perfluorinated hydrocarbon radical containing from 1 to 8 carbon atoms, x, y being integers comprised between 0 and 2, with at least $x + y = 1$ and $x + y$ is at most 2. It can also be used compounds having also some I or Br in the place of F of the perfluorinated hydrocarbon. These are known as polyiodided or polybrominated compounds. Moreover iodides and/or bromides of alkaline or alkaline-earth metals as described in European patent application No. 407937 can be used.

20 When the polymerization is over, the fluoroelastomer is isolated from the polymeric latex by known methods, such as coagulation by addition of electrolytes or by cooling.

25 The polymerization reaction is generally carried out at temperatures from 25°C to 150°C, under pressure up to 10 MPa.

The preparation of the elastomeric copolymers according to the invention can be carried out also by polymerization in the presence of a microemulsion formed by one or more perfluoropolyoxyalkylenes and water, according to the method described in European patent application No. 250767.

30 The polymerization can be carried out also by using, instead of a microemulsion, an emulsion or a dispersion of perfluoropolyoxyalkylenes and water according to the method described in USA patent No. 4789717.

Also the emulsions and dispersions of perfluoroxyalkylenes and water described for instance in European patent applications Nos. 196904, 280312 and 360292, can be used for this purpose.

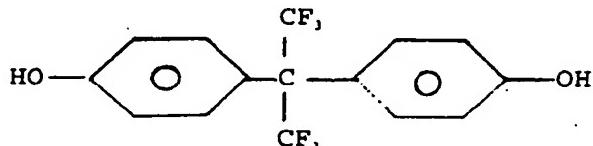
35 For the curing of the polymers of the invention the elastomeric composition must be heated under pressure, at a temperature from 130°C to 230°C, preferably from 160°C to 200°C, for a period of time comprised from 0.5 to 60 minutes and, preferably, from 1 to 15 minutes. The obtained articles can then be post-cured in stove or in oven, at atmospheric pressure, at a temperature from 130° to 300°C, preferably from 200°C to 275°C, for a period of time from 5 to 48 hours, and, preferably, from 10 to 24 hours.

The following examples are given for illustrative purpose but do not limit the scope of the present invention.

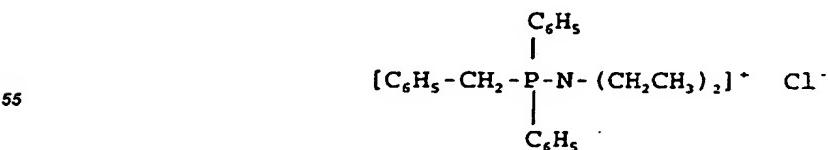
EXAMPLES

Preparation of the adduct

40 2 adducts according to the present invention are prepared by starting from the accelerator indicated below and from the bisphenol AF (BAF):



50 The accelerator has the following formula:



The preparation of the adduct produced starting from one accelerator mole and 5 (or 2 moles in case of 1:2 ratio, 3 moles for 1:3, and 4 moles for 1:4), moles of bisphenol AF gives the adduct in the molar ratio specified above.

- In a 10 l glass reactor, equipped with a dropping funnel and a stirrer, 352.8 g (1.05 moles) of bisphenol AF are dispersed under stirring into 5 l of water. A solution of 8.4 g (0.21 moles) of NaOH in 500 cc of water is then quickly dropped in the reactor. The reactor is kept under stirring at room temperature for 30 minutes. Then a solution of 80.5 g (0.21 moles) of amino-phosphonium dissolved in 800 cc of water is dropped under stirring in the reactor. A very thick suspension is obtained; it is kept under stirring at room temperature for 2 hours; then it is let to stay for about 4 hours. It is filtered on cloth and washed twice with overall 2 l of water. It is dried in a vacuum stove to 50-60°C for 20 hours and then the reaction mixture is brought to melt by heating at 100-120°C and it is allowed to cool, thus obtaining the adduct 1:5 according to the present invention.

EXAMPLES 1-3

- 15 In Table 1 the formulation of 3 compounds is reported, the first of which (compound No. 1) is a composition wherein an adduct according to the present invention was not used, but, separately, the accelerator and the bisphenol AF.

In the compounds 2 and 3 the adduct prepared according to the present invention was utilized.

- 16 The fluoroelastomer is TECNOFLON[®] TH 340 of Ausimont, vinylidene fluoride, hexafluoropropene and tetrafluoroethylene terpolymer having a Mooney viscosity ML (1+10) at 121°C equal to 58, whose composition is:

VDF 37% by weight

25

HFP 37% "

30

TFE 26% "

(Fluorine: 70% by weight)

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TABLE 1: FORMULATION OF THE COMPOUND

	Ex. 1 (cfr)	Ex. 2	Ex. 3
	(phr)	(phr)	(phr)
<hr/>			
10			
Fluoroelastomer TH 340	100	100	100
Bisphenol AF	2.7	-	-
15 Accelerator (I)	1.35	-	-
Adduct (II)	-	4.5	-
Adduct (III)	-	-	3.5
20 MgO	3	3	3
Ca(OH) ₂	6	6	6
25 MT Black	30	30	30
<hr/>			

Accelerators (I): [Ph₂P-N-(CH₂CH₃)₂]⁺Cl⁻
CH₂Ph

Adduct (II): molar ratio accelerator/bisphenol 1:3 obtained by melting the reaction mixture.

35 Adduct (III): 1:5 obtained by melting of the reaction mixture.

- 40
- Characterization of the compound of Table 1A
- 45 These blends were cured at 170°C in press and then to a post-curing in air stove between 200°C and 250°C for 24 hours.
- The curing evaluation was carried out by oscillating disc rheometer (ODR) of Monsanto type according to ASTM D 2084/81.
- 50 The data relating to the blends viscosity, the curing characteristics and the mechanical properties are reported in Table 1A.

Table 1A:

characteristics of th compound of Table 1.				
		Ex 1 (cfr)	Ex. 2	Ex. 3
5	<u>Rheometric properties</u>			
10	Mooney Viscosity (ASTM D1646-82)			
15	ML(1+10) at 121°C (Mooney)	106	82	103
20	Mooney Scorch at 135°C			
25	Minimum Viscosity (in Mooney)	44	32	45
30	Time for Increasing of 15 points the viscosity (min)	11'45"	33'20"	30'
35	ODR 12' at 177°C, Arc +/- 3° (ASTM D2084-81)			
40	ML (lbf-in)	16	13	16
45	MH (lbf-in)	72	108	96
50	ts2 (sec)	123	141	168
55	t90 (sec)	249	270	333
60	v _{max} (lbf-in/sec)	0.8	1.8	1.2
65	<u>Mechanical properties (ASTM D412-83)</u>			
70	Post cure @ 250°C x 8+16 hours			
75	Modulus 100% (MPa)	6.6	7.9	6.9
80	Tensile stress (MPa)	13.5	16	15.5
85	Elongation at break (%)	228	181	219
90	Hardness Shore A	82	82	85
95	Compression Set 70 h at 200°C (ASTM D 395 Method B) O-rings 214 (%)	66	31	32

From the above results it is noticed that the viscosity decreases by indicating an improved processability; the scorch increases therefore indicating a greater compound safety; the curing (ODR) shows a greater crosslinking yield (MH) and higher curing rate (v_{max}). The balance of the mechanical properties is surprisingly very satisfactory: a higher tensile stress/elongation ratio is obtained. The compression set is unexpectedly improved to a great extent.

EXAMPLES 4-5

Examples 1-3 were repeated using a fluoroelastomer TECNOFLO- N[®] T428E of Ausimont: terpolymer of vinylidenefluoride, hexafluoropropene and tetrafluoroethylene, having a Mooney ML (1+10) viscosity at 121°C equal to 20, whose composition is:

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VDF	45% by weight
HFP	33% by weight
TFE	22% by weight

5

(Fluorine: 68.5% by weight); $[\eta]_{\text{MEK}}^{30^\circ\text{C}} = 55$ (intrinsic viscosity).

The formulations are reported in Table 2 and the characteristics are reported in Table 2A.

10

TABLE 2:

15

<u>COMPOUNDS FORMULATION</u>		
	EX. 4 (cfr)	EX. 5
	(phr)	(phr)
Fluoroelastomer NMA2	100	100
Bisphenol AF	1.5	-
Accelerant (I)	0.6	-
Adduct (II)	-	2
MgO	3	3
Ca(OH) ₂	6	6
MT Black	30	30

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TABLE 2A:

characteristics of the compound of Table 1.			
		Ex. 4 (cfr)	Ex. 5
5	<u>Rheometric properties</u>		
10	Mooney Viscosity (ASTM D 1646-82)		
15	ML(1+10) at 121°C (in Mooney)	39	39
20	Mooney Scorch at 135°C		
25	Minimum Viscosity (in Mooney)	14	13
30	Time for increasing of 15 points the viscosity (min)	37'30"	40'30"
35	ODR 12' at 177°C Arc +/- 3° (ASTM D2084-81)		
40	ML (lbf·in)	4	4
45	MH (lbf·in)	44	52
50	ts2 (sec)	195	168
55	t90 (sec)	285	237
60	v _{max} (lbf·in/sec)	0.8	1.4
65	<u>Mechanical properties (ASDTM D412-83)</u>		
70	Post curing @ 250°C x 8+16 hours		
75	Modulus 100% (MPa)	2.5	4.0
80	Tensile strength (MPa)	12	14
85	Elongation at break (%)	329	286
90	Hardness Shore A	63	62
95	Compression Set 70h at 200°C (ASTM D 395 Method B) O-rings 214 (%)	54	34
100	Compression Set 70h at 23°C O-rings 214 (%)	44	30

45 The results show the same previous trends, in particular as regards the curing rate (v_{max}), compression set and the improved balance of the mechanical properties.

EXAMPLES 6-7

50 Examples 1-3 were repeated with the fluoroelastomer indicated below; the formulations are reported in Table 3 and the characteristics in Table 3A.
High fluorine tetrapolymer TECNOFLON^(R) LX 5291 having composition:

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VDF 32% by weight
 HFP 30% "
 5 MVE 7% " (perfluoromethylvinylether)
 TFE 31% "
 10 (Fluorine 70% ") , ML(1+10) at 121°C = 31.

TABLE 3:

COMPOUND FORMULATION			
	EX. 6 (cfr)	EX. 7	
	(phr)	(phr)	
15	Fluoroelastomer	100	100
20	Bisphenol AF	2.7	-
25	Accelerant (I)	1.35	0.3
30	Adduct III	-	3.5
	MgO	3	3
	Ca(OH) ₂	6	6
	MT Black	30	30

35

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60

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TABLE 3A:

		characteristics of the compound of Table 3.	
		Ex. 6 (cfr)	Ex. 7
Rheometric properties			
Mooney Viscosity (ASTM D 1646-82)			
10	ML(1+10) at 121°C (in Mooney)	78	74
ODR 12' at 177°C Arc +/-3° (ASTM D2084-81)			
15	ML (lbf-in)	10	9
MH (lbf-in)	54	77	
ts2 (sec)	225	246	
t90 (sec)	350	390	
20	v _{max} (lbf-in/sec)	0.5	1.1
Mechanical properties (ASDTM D412-83)			
25	Post curing @ 250°C x 8+16 hours		
Modulus 100% (MPa)	5.3	6.0	
Tensile strength (MPa)	11	13	
30	Elongation at break (%)	220	203
Hardness Shore A	79	81	
35	Compression Set 70h at 200°C (ASTM D 395 Method B) O-rings 214 (%)	63	30

By comparing the results it is noted the same trend of the previous examples: an improved processability (lower Mooney of the compound); improved crosslinking yield (MH) and crosslinking rate (v_{max}); the balance of the mechanical and elastomeric properties shows a clear improvement.

Claims

- 45 1. Curable fluoroelastomeric compositions comprising:
 - A) 100 phr copolymers or terpolymers based on VDF having a content in fluorine of at least 67% by weight, the VDF being comprised from 30 to 50% by weight, from 20 to 60% by weight of HFP, optionally other monomeric units deriving from a monomer having ethylene unsaturation; the sum of the comonomers being 100;
 - B) from 1 to 5 phr of an adduct between an accelerator and a curing agent in molar ratio from 1:2 to 1:5, the accelerator being an onio-organic compound having a positive charge, the curing agent being a di- or polyhydroxy or di- or polythiol compound; the adduct being obtained by melting of the reaction product between accelerator and curing agent in the indicated molar ratios, or by melting of the adduct mixture 1:1 added with the curing agent in the indicated amounts; optionally
 - C) the accelerator indicated in B) in amounts from 0.05 to 0.5 phr.
2. Compositions according to claim 1 wherein the other monomeric units are from 0 to 30% by weight of

TFE and from 0 to 40 by weight of perfluoroalkylvinylethers.

3. Compositions according to claims 1 and 2 wherein B) ranges from 2 to 4.5 phr and the adduct is 1:2 or 1:3.
5. 4. Compositions according to claims 1-3 wherein the accelerator forming the adduct cation is selected from the following classes:
 - I) aminophosphonium $[P(NR'R'')_n(R^1 R^2 R^3)_{4-n}]^+$
wherein n is an integer from 1 to 3;
 - 10 R', R'' and R¹ R² R³, equal or different from each other, are alkylic, cycloalkylic, arylic, arylalkylic, oxy-alkylic or polyoxyalkylic groups having a free or esterified terminal -OH function;
R' and R'' contain from 1 to 7 carbon atoms and can be linked each other so as to form an heterocyclic ring with the nitrogen atom while R¹, R², R³ equal or different from each other contain from 1 to 18 carbon atoms;
 - 15 II) compounds having the formula $Q^+(R^a R^b R^c R^d)_4$
wherein Q is selected from nitrogen, phosphorus, arsenic, antimonium;
 - III) compounds having formula: $S^+(R^a R^b R^c)_3$
- 20 wherein in II) and III) R^a, R^b, R^c, R^d are selected from alkyls, aryls, alkylaryls or their combinations, two of said free radicals can be linked each other and the Q or S atom can form an heterocyclic ring.
- 25 5. Compositions according to claim 4 wherein the accelerator is selected from the quaternary phosphonium compounds containing at least a phosphorus atom linked with four simple covalent bonds to four organic radicals, the organic radicals generally containing from 2 to 8 carbon atoms, the organic radical, being linear or branched, optionally containing heteroatoms; or from aminophosphonium derivatives wherein the phosphorus atom is linked to a nitrogen atom and the other three covalent bonds are organic radicals wherein the carbon is linked to the phosphorus.
- 30 6. Compositions according to claims from 1 to 5 wherein the anion obtained from the curing agent is selected from the polyhydroxy or polythiol compounds from the following classes:
 - X1) A(BH)_m
wherein A is an arylene radical optionally substituted with alkylic groups, such radical including optionally alkyl groups has from 6 to 14 carbon atoms, B is oxygen or sulphur and m is equal to 2 or 3;
 - 35 X2) HB-R^{4a}-BH
wherein R^{4a} is an alkylene or cycloalkylene radical optionally substituted with alkylic groups, such radical including optionally alkyl groups has from 6 to 18 carbon atoms and B is oxygen or sulphur;
 - X3)
- 40
- 45 wherein R^{2a} is -SO-, -SO₂-, -CO- or a linear or branched alkylene radical containing from 1 to 9 carbon atoms and wherein the H atoms can be partially or wholly substituted with F atoms;
- 50 X4) HOCH₂-R^{3a}-CH₂OH
wherein R^{3a} is a perfluoropolyether or polyfluoroether chain, the average molecular weight by number Mn being from 360 to 2,000.
- 55 7. Curable compositions according to claims from 1 to 6 wherein to obtain the cured product it comprises:
 - a) one or more acceptors of inorganic acids selected from those known in ionic vulcanisation of vinylid n fluoride copolymers, in amounts 1-40 parts for 100 parts fluoroelastomeric copolymer;
 - b) one or more basic compounds selected from those known in ionic curing of vinylidene fluoride copolymers, in amounts from 0.5 to 10 parts for 100 parts fluoroelastomeric copolymer.

8. Curable compositions according to claims 1 and 2 wherein is present also an olefin in amounts from 0 to 25% by weight as ethylenically unsaturated monomer.

9. Curable compositions according to claims from 1 to 7 wherein the monomeric composition by weight is:

VDF	40-50%
HFP	50-60%.

10. Curable compositions according to claims 1-7 wherein the monomeric composition by weight is:

VDF	30-50%
HFP	20-60%.
TFE	10-30%.

11. Curable composition according to claims 1-7, wherein the monomeric composition by weight is:

VDF	30-47%
HFP (hexafluoropropene)	20-40%
PAVE	3-20%
TFE	10-30%.

12. Curable compositions according to claim 8, wherein the monomeric composition by weight is:

VDF	30-50%
HFP	20-58%
PAVE	0-40%
ethylene	2-15%
TFE	0-30%.

13. Use of the compositions according to claims 1-12 for preparing fuel hoses and shaft seals.

14. Use of the compositions according to claims 1-12 for preparing O-rings for injectors.

15. Use according to claims 13 and 14 wherein the fluoroelastomeric compositions are those of claim 10.

16. Adduct between an accelerator and a curing agent in molar ratio from 1:2 to 1:5, the accelerator being an onto-organic compound having a positive charge, the curing agent being a di- or polyhydroxy or di- or polythiol compound; the adduct being obtained by melting of the reaction product between accelerator and curing agent in the indicated molar ratios, or by melting of the adduct mixture 1:1 added with the curing agent in the indicated amounts.

17. Adduct according to claim 16, wherein the cation is selected from the classes of claim 4 and the anion from the compounds of claim 6.



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EUROPEAN SEARCH REPORT

Application Number
EP 95 10 8042

DOCUMENTS CONSIDERED TO BE RELEVANT															
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)												
X	EP-A-0 333 062 (DU PONT DE NEMOURS AND COMPANY) 20 September 1989 * claims; example 21 *	1-17	C08K5/00 C08L27/12 C08K5/19 C08K5/37 C08K5/50 C08K5/5399												
A	US-A-5 262 490 (KOLB, ROBERT E. ET AL.) 16 November 1993 * column 7, line 25 - line 40; claims; table 2 *	1													
A	EP-A-0 404 411 (MINNESOTA MINING & MFG) 27 December 1990 * page 13, line 1 - line 6; claims *	1													
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A	EP-A-0 335 705 (MINNESOTA MINING & MANUFACTURING COMPANY) 4 October 1989 * claims; examples 22-26 *	1													
A	CHEMICAL ABSTRACTS, vol. 113, no. 12, 17 September 1990 Columbus, Ohio, US; abstract no. 99190, * abstract * & JP-A-01 315 449 (NIPPON MECTRON, LTD.) 20 December 1989	1													
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			TECHNICAL FIELDS SEARCHED (Int.Cl.)												
			C08K C08L												
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search</td> <td>Date of completion of the search</td> <td>Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>4 September 1995</td> <td>DE LOS ARCOS, E</td> </tr> <tr> <td colspan="3">CATEGORY OF CITED DOCUMENTS</td> </tr> <tr> <td colspan="2"> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background P : non-written disclosure I : intermediate document </td> <td> T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons O : member of the same patent family, corresponding document </td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	4 September 1995	DE LOS ARCOS, E	CATEGORY OF CITED DOCUMENTS			X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background P : non-written disclosure I : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons O : member of the same patent family, corresponding document
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	<p>CHEMICAL ABSTRACTS, vol. 99, no. 18, 31 October 1983 Columbus, Ohio, US; abstract no. 141361, * abstract *</p> <p>& KAUCH. REZINA, vol. 7, 1983 MOSCOW, USSR, pages 13-15,</p> <p>NUDEL'MAN, Z.N. ET AL. 'Reason for the accumulation of compression set by SKF-26-bisphenol vulcanizates'</p> <p>-----</p> <p>CHEMICAL ABSTRACTS, vol. 93, no. 25, 22 December 1980 Columbus, Ohio, US; abstract no. 239650, * abstract *</p> <p>& JP-A-55 108 884 (NIPPON OIL SEAL INDUSTRY CO., LTD.) 21 August 1980</p> <p>-----</p>	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
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CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>	
<small>EPO FORM 150 (CAT. 1991)</small>			